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# PROGRAM AND ABSTRACTS OF PAPERS CITRUS RESEARCH CONFERENCE

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FRUIT AND VEGETABLE

CHEMISTRY LABORATORY

263 SOUTH CHESTER AVENUE

PASADENA, CALIFORNIA 91106

December 3, 1968

Western Utilization Research and Development Division
Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE



### FOREWORD

This Citrus Research Conference is being held to bring to members of the citrus and allied industries in Southern California and Arizona the latest results of research on the chemistry, pharmacology, and technology of citrus fruits and their products carried on by the Utilization Research and Development Divisions of the Agricultural Research Service, U. S. Department of Agriculture. The following are participating in this year's conference.

- Western Utilization Research and Development Division:
  - Western Regional Research Laboratory (Division headquarters), 800 Buchanan Street, Albany, Calif. 94710
  - Fruit and Vegetable Chemistry Laboratory, 263 South Chester Avenue, Pasadena, Calif. 91106
- Southern Utilization Research and Development Division:
  - U. S. Fruit and Vegetable Products Laboratory,
     600 Avenue S, N.W., Winter Haven, Florida 33882
  - Food Crops Utilization Research Laboratory P.O.Box 388, Weslaco, Texas 78596

# PROGRAM

# CITRUS RESEARCH CONFERENCE

# Tuesday, December 3, 1968

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### OXYGENATED COMPOUNDS IN CITRUS OILS

# M. G. Moshonas and Eric D. Lund

Southern Utilization Research and Development Division U.S. Fruit and Vegetable Products Laboratory Winter Haven, Florida

The careful analysis of citrus oils by gas-liquid chromatography (GLC) that began in 1962 at the Winter Haven laboratory has been extended to include the alcohol fractions of various citrus oils and the "carbonyl" fraction of Valencia orange oil. A relatively complete picture of the constitution of the volatile portion of Valencia orange oil is now available. A study of the "carbonyl" fraction of grapefruit oil is now underway and studies of this fraction in other citrus oils (lemon, lime and tangerine) are planned in order to complete the picture as far as the composition of the volatile portion of these oils is concerned.

The isolation procedure used for the alcohols involved liquid-liquid extraction with either a carbon tetrachloride-propylene glycol pair or with glycerol alone, followed by a rough fractionation on alumina and finally GLC analysis with Carbowax 30M as the liquid phase. The "carbonyl" fractions were isolated by vacuum fractional distillation followed by chromatographic separation on alumina and a final GLC analysis on Carbowax 20 M of the fractions from the alumina column.

Because of suspected losses of material during the isolation procedure, an exact quantitative analysis was not obtained; however, a rough quantitative estimate of the major components based on the relative size of the GLC peaks was made, and a list of these compounds is included in the following table:

| Grape-                |        |       |       |      |           |  |  |  |
|-----------------------|--------|-------|-------|------|-----------|--|--|--|
| Compound              | Orange | fruit | Lemon | Lime | Tangerine |  |  |  |
| Linalool              | X      | X     | X     | X    | X         |  |  |  |
| Octanol               | X      | X     | X     | X    | X         |  |  |  |
| Terpinene-4-ol        |        |       | X     | X    |           |  |  |  |
| $\alpha$ -Terpineol   | X      | X     | X     | X    |           |  |  |  |
| Decanol               | X      | X     |       |      |           |  |  |  |
| Citronellol           |        |       |       |      | X         |  |  |  |
| Nerol                 | X      |       | X     | X    | X         |  |  |  |
| Trans-carveol         | X      | X     |       |      |           |  |  |  |
| 1,8-p-Methadiene-9-ol | X      |       |       |      | X         |  |  |  |
| Elemol                |        | X     |       |      |           |  |  |  |
| Thymol                |        |       |       |      | X         |  |  |  |
| 8-p-Menthene-1,2-diol |        |       |       |      | X         |  |  |  |

The most abundant constituents of the "carbonyl" fraction of Valencia orange oil were found to be n-octanal, n-nonanal, citronellal, n-decanal, neral, geranial, carvone, nootkatone,  $\beta$ -sinensal and  $\alpha$ -sinensal, as estimated from the relative size of the peaks in the gas-liquid chromatogram.

With the completion of the analysis of the alcohol fraction of all of the citrus oils and the "carbonyl" fraction of orange oil, it is now possible to make some limited generalizations about the relative contribution of various consituents to the flavor and odor of the oil. The alcohol fractions in general do not seem to possess the basic flavor or odor of the citrus. Many of the major alcohol constituents are identical in the various oils; for instance, linalool, octanol, and  $\alpha$ -terpineol are found in major amounts in all of them. In the case of orange, the alcohol fraction seems to contribute a rich, full-bodied, smooth quality to the aroma, while the "carbonyl" fraction possesses the more essential elements of the aroma and flavor. The hydrocarbon fraction of Valencia oil which was analyzed in an earlier study appears to be a relatively minor contributor to the flavor.

The authors acknowledge the contribution of Dr. G. L. K. Hunter who participated in the work on the alcohols.

# AROMA CONCENTRATION FOR DEHYDRATED ORANGE POWDER

John L. Bomben, D. G. Guadagni, and J. G. Harris

Western Utilization Research and Development Division Western Regional Research Laboratory Albany, California

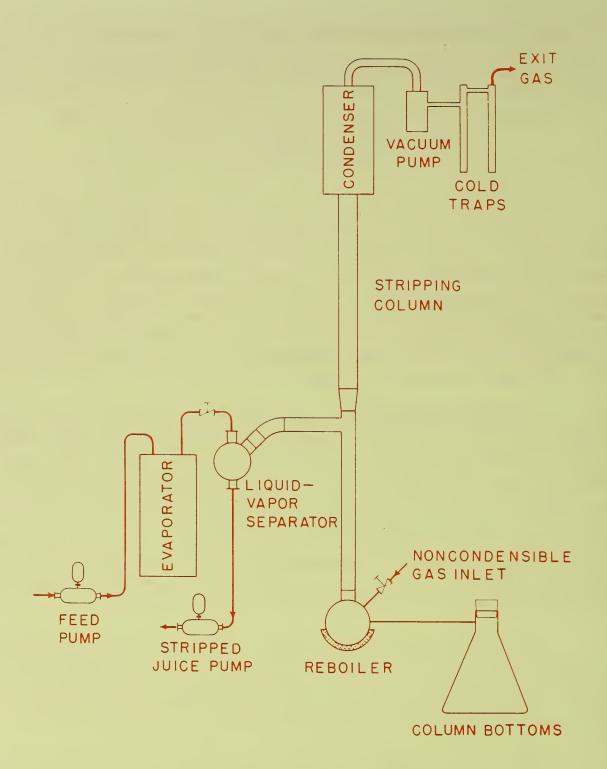
During dehydration orange juice undergoes loss of volatile flavor compounds. Efforts have been made to determine conditions under which volatiles might be retained; however, the approach used commercially is to add back the lost volatiles to the final product. Encapsulation of the aroma compounds in amorphous sugar is a well established technique. Peel oil provides a concentrated, nonaqueous source of aroma. It has been found however that peel oil cannot provide all the aroma of fresh orange juice. It is thought that some of the aroma is supplied by water-soluble compounds that are in the juice but not in the peel.

A technique has been developed for making aroma concentrates from fresh fruit juices suitable for adding to a dehydrated product. This process is a modification of the WURVAC process developed at our Laboratory several years ago. It consists of vacuum stripping of juice with nitrogen. The aromas are separated from evaporated water in a rectifying column. An ice-point condenser returns all the water to the top of the column and water leaves only from the column bottom. Aromas are collected downstream from the ice-point condensers in a cold trap. The aroma concentrates are 1000-fold water solutions which can be directly condensed on a dehydrated product or dry carrier such as sugar or dextrin.

Experiments with orange, apple, and tomato juices were conducted in a small pilot-plant unit. Material balances made on this process by gas-liquid chromatography and odor threshold showed a high recovery of the volatile compounds in the aroma concentrate. Only small amounts of material were lost in the other streams leaving the process.

When orange aroma was condensed directly on a foam-mat dried orange powder, a substantial amount of fresh orange aroma was added with only a small increase in moisture.

A schematic diagram of the process is shown on page 8.



# RECENT PROGRESS IN THE BIOCHEMISTRY OF CITRUS BITTER PRINCIPLES

V. P. Maier and Shin Hasegawa

Western Utilization Research and Development Division Fruit and Vegetable Chemistry Laboratory Pasadena, California

Citrus juices sometimes have unpleasant flavor due to substances that impart excessive bitterness. Two classes of compounds are generally responsible, namely limonoids and flavanone glycosides. Until recently, it was believed that the bitterness of grapefruit juice was caused entirely by the bitter flavanone glycosides (particularly naringin). However, in 1965 we found that grapefruit juice frequently contains significant amounts of the intensely bitter limonoid called limonin (Maier and Dreyer, J. Food Sci. 30:874-75, 1965). Limonin has long been known to be responsible for the bitterness of navel orange juice. More recently, we have found limonin to be present in laboratory-processed juice samples of yellow-ripe lemons and in commercial concentrated juice made from lemons grown in Arizona, California, and Florida. In all instances the juices were judged to be bitter in taste. Of the three major types of citrus juices produced commercially, grapefruit juice is subject to bitterness from both flavanone glycosides and limonoids, whereas orange and lemon juices are subject only to limonoid bitterness.

An important distinction between the two types is that flavanone glycoside bitterness occurs in both intact fruit and juice, whereas limonin bitterness occurs only in juice. The edible portion of the intact fruit when eaten fresh is nonbitter. In addition, limonin bitterness takes time to develop after the juice is prepared. This phenomenon is frequently referred to as "delayed bitterness."

In recent years, we have been studying the biochemistry of limonin in an effort to understand the mechanism of delayed bitterness. Last year we reported that limonin itself does not occur in the edible tissue of intact citrus fruits. Instead a nonbitter precursor of limonin is found (Maier and Beverly, J. Food Sci. 33:488-92, 1968). This nonbitter precursor has now been identified as limonoate A-ring lactone (Maier and Margileth, Phytochem. 7, 1968, in press). It is found in the structural tissues of the endocarp and in the albedo of the peel of certain mature navel oranges, grapefruit, and lemons. Also, limonoate A-ring lactone is readily converted into limonin in solutions having the same acidity as orange juice. Therefore, in juice manufacture when the broken tissues of the fruit mix with the acidic juice, the nonbitter limonoate A-ring lactone, which is unstable under these

conditions, is converted to the bitter compound limonin, and the juice becomes bitter. If the juice is heated, the rate of conversion of the nonbitter precursor to limonin is increased, and the juice becomes bitter more rapidly.

During work on the identification of the limonoate A-ring lactone a new enzyme was discovered in citrus fruit tissue extracts which catalyzes the conversion of limonoate A-ring lactone to limonin in acidic solutions such as citrus juices (Maier, Hasegawa and Hera, Phytochem. 7, 1968, in press). However, in neutral to alkaline solutions—such as the cytoplasm of cells, the enzyme (which was named limonin D-ring-lactone hydrolase) catalyzes the hydrolysis of limonin to limonoate A-ring lactone. This enzyme appears to be the missing link needed to account for the presence of limonoate A-ring lactone and the absence of limonin in the tissues of intact citrus fruits--that is, the absence of bitterness of fresh navel orange as contrasted with the bitterness of its juice.

Studies are continuing on limonin D-ring-lactone hydrolase and other enzymes involved in the biochemistry of citrus bitter principles. We are convinced that knowledge of these enzymes will aid in the task of devising methods for controlling excessive bitterness in citrus fruit and juices.

Carl Vandercook, Ruth Price and H. C. Guerrero

Western Utilization Research and Development Division Fruit and Vegetable Chemistry Laboratory Pasadena, California

The authenticity (or juice content) of citrus products is important to the citrus industry and consumers. Because of the success of the statistical, multiple-analysis approach with lemon juice reported last year, it was decided to include other citrus juices. Many chemical criteria of authenticity, such as inorganic constituents, have been proposed for orange juice, but none has been completely satisfactory. Further inorganic compounds can be easily and cheaply added to counter any dilution of the natural juice.

Phosphorus is one of the better inorganic parameters. It is associated with many biochemically important classes of compounds, such as nucleic acids and phospholipids. Since these compounds would be too expensive to use as adulterants, we attempted to further characterize citrus juices by their organic phosphorus compounds, such as the phospholipids and ethanol-insoluble phosphorus (EIP) including the nucleic acids, phosphoproteins, and inorganic and total phosphorus.

The analytical procedures for the group separations--mostly adapted from published methods--will be discussed briefly. Averages of data for the phosphorus fractions and supplemental analyses for orange, lemon, and grapefruit juices are given in the following table. The values in parentheses are the coefficients of variation ( $\sigma/\bar{x} \cdot 100$ ).

|       | Citrica           | Amino   | Phen-b   | Total <sup>c</sup>   | Inorg.   | 0   | Lipid <sup>c</sup>  |
|-------|-------------------|---|--|--|--|---|---|
| Brix  | acid              | acids   | olics  | P  | P  | EIP   | P   |
| 12.9  | 13.1              | 2.82  | 0.823  | 19.3   | 12.6   | 3.02  | 1.41  |
| (6.3) | (18.2)            | (19.5)  | (16.0)   | (12.8)   | (23.1)   | (26.1)  | (17.7)  |
|       | 89.8              | 1.80  | 0.744  | 11.1   | 6.10   | 1.94  | 1.29  |
|       | (8.0)             | (15.0)  | (37.0)   | (22.1)   | (27.9)   | (35.1)  | (39.5)  |
| 11.4  | 19.6              | 2.04  | 1.121  | 13.6   | 9.45   | 1.49  | 1.08  |
| (8.2) | (13.0)            | (7.0)   | (32.0)   | (16.8)   | (15.6)   | (37.3)  | (23.6)  |
|       | 12.9<br>(6.3)<br> | Brix acid 12.9 13.1 (6.3) (18.2) 89.8 (8.0) 11.4 19.6 | Brix acid acids 12.9 13.1 2.82 (6.3) (18.2) (19.5) 89.8 1.80 (8.0) (15.0) 11.4 19.6 2.04 | Brix acid acids olics 12.9 13.1 2.82 0.823 (6.3) (18.2) (19.5) (16.0) 89.8 1.80 0.744 (8.0) (15.0) (37.0) 11.4 19.6 2.04 1.121 | Brix         acid         acids         olics         P           12.9         13.1         2.82         0.823         19.3           (6.3)         (18.2)         (19.5)         (16.0)         (12.8)            89.8         1.80         0.744         11.1           (8.0)         (15.0)         (37.0)         (22.1)           11.4         19.6         2.04         1.121         13.6 | Brix         acid         acids         olics         P         P           12.9         13.1         2.82         0.823         19.3         12.6           (6.3)         (18.2)         (19.5)         (16.0)         (12.8)         (23.1)            89.8         1.80         0.744         11.1         6.10           (8.0)         (15.0)         (37.0)         (22.1)         (27.9)           11.4         19.6         2.04         1.121         13.6         9.45           (8.2)         (13.0)         (7.0)         (32.0)         (16.8)         (15.6) | Brix         acid         acids         olics         P         P         E I P <sup>c</sup> 12.9         13.1         2.82         0.823         19.3         12.6         3.02           (6.3)         (18.2)         (19.5)         (16.0)         (12.8)         (23.1)         (26.1)            89.8         1.80         0.744         11.1         6.10         1.94           (8.0)         (15.0)         (37.0)         (22.1)         (27.9)         (35.1)           11.4         19.6         2.04         1.121         13.6         9.45         1.49 |

aMeq./100 ml. juice. bAbsorbance of 1:20 dilution with ethanol. CMg.P/100 ml. juice.

Several interesting observations were noted from the analyses of the samples. One was that the phospholipids and EIP fractions are both largely present in the insoluble cloud portion of the juice. Secondly, an inverse correlation was noted between the percentages of EIP and inorganic P, which could be useful in detecting an adulterated sample.

In considering the coefficients of variation for the individual analyses, none would be very sensitive for detecting additives if used alone. However, by use of a statistical approach to the problem and various combinations of analyses, a practical method of detecting adulteration should be possible. One promising statistical approach will be discussed.

### CAROTENONES AND THEIR RELATION TO CITRUS COLOR

Henry Yokoyama and H. C. Guerrero

Western Utilization Research and Development Division Fruit and Vegetable Chemistry Laboratory Pasadena, California

Color of ripe citrus fruits has long been identified with a class of pigments known as carotenoids. An exception is the blood orange. Earlier studies of the pigments of commercial fruits such as grapefruit and oranges indicated that color is due in large part to commonly occurring carotenoids, such as lycopene,  $\beta$ -carotene, violaxanthin, and cryptoxanthin. Some investigators have also reported trace amounts of apo-carotenals ( $\beta$ -apo-8'-carotenal and  $\beta$ -citraurin) in oranges. Until very recently the known keto-carotenoids were restricted to animals and to plants other than citrus. After the isolation and structural identification of the interesting methyl ketones (citranaxanthin, reticulataxanthin (I) and sintaxanthin) the role of these apo-carotenones became evident, namely to impart rich red color to such citrus

fruits as tangerines, Minneola tangelos, Temple oranges, and Sinton citrangequats. In the trigeneric hybrids, the apo-carotenones appear as the dominant pigments, increasing generally from monogeneric to bigeneric to trigeneric hybrids. Investigations in our laboratory on the natural occurrence of these apo-carotenones reveal their ubiquitous nature among citrus fruits. Stage of maturity in grapefruit and lemons determines their absence or presence.

Until very recently, known keto-carotenoids invariably contained conjugated keto-groups. Semi- $\beta$ -carotenone (II) and  $\beta$ -carotenone (III), which

were isolated and structurally identified in our laboratory, were found to contain unconjugated keto-groups. As indicated previously these carotenones are responsible for the intense color and are the main pigments of the fruit of the citrus relatives Triphasia trifolia and Murraya exotica. Two additional new naturally occurring carotenones were isolated recently in our laboratory from citrus relatives. These latter carotenones contain decaenone and nonaenone chromophores. Their structures, biological significance, and role in citrus color will be discussed in detail.

# EFFECT OF SUBSTITUENTS ON THE TASTE OF FLAVANONES AND DIHYDROCHALCONES

### Robert Horowitz and Bruno Gentili

Western Utilization Research and Development Division Fruit and Vegetable Chemistry Laboratory Pasadena, California

After relation between bitterness and chemical structure of citrus flavanones had been established, various modifications in these compounds were made in order to pinpoint some of the major structural requirements for taste. These modifications have taken the following forms: (1) removal of large fragments of the molecule; (2) conversion of the flavanone aglycone into other flavonoid types; and (3) alteration of substituent groups. In general, modifications of types 1 or 3 give rise only to quantitative changes in the existing taste, while modifications of type 2 may give rise to qualitative changes in certain cases. In this talk we will be concerned mainly with modifications of type 3.

From results obtained by altering the sugar portion of these molecules we conclude that (1) neither the C-2 nor C-6 hydroxyl group of glucose is required for taste, (2) the structural features most directly involved in taste are the C-3 and C-4 hydroxyl groups of glucose, and (3) a bulky substituent, such as  $\underline{L}$ -rhamnosyl, can have opposing effects depending on which hydroxyl group of glucose it is attached to.

The effect of substituents attached to the aromatic rings of these compounds is difficult to interpret although certain broad conclusions are possible. A summary of the available results will be given.

# FLAVANONE ACCUMULATION IN GRAPEFRUIT AS INFLUENCED BY TIME OF FRUIT-SET

Roger F. Albach and George H. Redman

Southern Utilization Research and Development Division Food Crops Utilization Research Laboratory Weslaco, Texas

The effect of fruit age and time of fruit-set on the flavanone content of whole Texas-grown grapefruit was investigated. Beginning in May, monthly samplings were made from three groups of fruit from the same tree but representing three different dates of fruit-set. The fruit had been set during the normal March blossoming period of the prior year (fruit age, 13+ months), during an off-bloom of the previous December (5+ months), or during the normal bloom of the preceding April (1+ month).

Thin layer chromatography (TLC) fluorometric analyses were made of the six major flavanones found in grapefruit: naringen, naringenin-7-rutinoside, neohesperidin, poncirin, and isosakuranetin-7-rutinoside.

Initially, the naringin content of the December-set fruit was approximately 40 percent greater than that of the April set, but this difference decreased to 35 percent by January. Both the December-set and April-set fruit showed a maximium of naringin content in July. From November through the harvest season, the December-set fruit had a naringin content approximately constant at 1200 mg./fruit while the April-set fruit had a content near 900 mg./fruit.

These and other flavanone compositional changes characteristic of citrus will be discussed.

# APPLICATION OF NEW PROCESSING TECHNIQUES TO DESERT GRAPEFRUIT PRODUCTS\*

F. E. Nelson, W. C. Brown, R. A. Khalifah, G. A. Crevasse and R. H. Manley

Arizona Agricultural Experiment Station The University of Arizona Tucson, Arizona

Products previously prepared from grapefruit juice in combination with other fruit juices and purées have been studied in an attempt to improve them and to devise modifications of potential commercial interest.

High acidity, particularly in early season fruit, limits acceptability of juice blends. Reducing titratable acidity to 1.15-1.20 percent as citric acid (pH 3.4-3.6) by addition of food-grade calcium carbonate and removal of the precipitated calcium citrate resulted in a product of high acceptability. Adjustment to 16.5° Brix with added sugar or equivalent sweetness with a combination of calcium cyclamate and sodium saccharin increased acceptability of this product. In combination with other juices and purées, the adjusted juice was considerably more acceptable.

Because of poor color retention and decline in flavor when grapefruit-strawberry or grapefruit-raspberry combinations were held at 75° or 98°F. (and also some deterioration at 35°F.), type of container and effect of several additives potentially inhibitory to such deteriorations were tested. Ascorbic acid, propyl gallate, sodium sulfite, carboxymethylcellulose, low-methoxy pectin, locust bean gum, gum arabic, gum tragacanth, and rice starch were ineffective. Lacquered cans and brown glass bottles with crown caps were the most effective; tinned cans and several types of plastic containers were less satisfactory.

Commercial concentrates of grapefruit juice and most single strength canned juices have been too bitter for combination with other juices. Juice extracted carefully to minimize incorporation of albedo and membrane material and quickly filtered to remove rag and tissue fragments was concentrated in a rotary film evaporator and also freeze-dried. When reconstituted to single-strength juice both types were considerably less bitter than commercial concentrates. Slow freezing left a core of concentrated juice which was low in bitterness and retained flavor well when reconstituted to single strength. Controlled fractional crystallization by freezing should be tried, but equipment for this needs to be developed.

<sup>\*</sup>Research conducted under Contract No. 12-14-100-8956(74) with U. S. Department of Agriculture, Agricultural Research Service.

Cottage cheese whey could not be combined with grapefruit juice at any potentially desirable level, regardless of sweetness or acidity because the whey flavor was too pronounced. Whey at 30-40 percent levels combined satisfactorily with grapefuit-based drinks containing red raspberry, strawberry, peach and apricot at levels of 7.5, 12.0, 25.6 and 25.6 percent respectively, when cerelose was added to give Brix values of approximately 23°. Equivalent sweetness from a combination of non-caloric sweeteners also was satisfactory.

Carbonated fruit-flavored drinks, mostly at 12° Brix or with equivalent non-caloric sweetener added and containing 4:1 grapefruit concentrate equivalent to 30 to 34 percent of fresh juice, received fairly good consumer acceptance. Had better grapefruit material been available, the acceptance undoubtedly would have been appreciably better.

Because bitterness of juice is a recurrent problem in formulating products, attention has been given to determination of the major bitter principles, naringin and limonin, in juice and the component portions of the fruit. A dry-column chromatography procedure has been developed to obtain adequate quantities of highly purified naringin for standards, as naringin prepared by previously used procedures was too impure for this use, based upon chromatographic evaluation. For determination of both naringin and limonin in tissues, a procedure involving addition of a cellulosic material (Solka-Floc) was essential during the extraction period to prevent formation of stable emulsions and permit quantitative recovery of the bitter principles. For limonin, the TLC procedure of Maier and Dreyer (J. Food Sci. 30:874-75, 1965) was used, except that final color development was in an iodine vapor atmosphere, resulting in greater sensitivity below 10 p.p.m. Naringin values in juice decrease from January to June, declining from 350-400 p.p.m. to 210-250 p.p.m. in the three series studied. Limonin values also tend to decline from the 8-10 p.p.m. level to as low as 3+ p.p.m. In mature fruit, albedo and segmental membranes are very high in naringin, whereas juice sacs tend to have about double the level of naringin found in juice. Juice sacs have 2-4 times as much limonin as does juice, membranes one-half to one-fourth the level of juice, and albedo only trace amounts. All components of immature fruit are high in naringin, and data are being collected on the changes associated with maturation. Some of the problems of bitterness undoubtedly are associated with extraction of naringin and limonin from grapefruit tissues.

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Fruit and Vegetable Chemistry Laboratory 263 South Chester Avenue, Pasadena, California 91106

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<sup>\*</sup>Reprints are available at the addresses indicated; patents are available only by purchase at 50¢ a copy from the U.S. Patent Office, Washington, D. C. 20250.

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